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ABSTRACT

Experimental intensity ratios of Auger transitions $L_3 M_{4,5} M_{4,5}$ /$L_2 M_{4,5} M_{4,5}$ for Co, Ni, Cu, and Zn ($27 \leqslant Z \leqslant 30$) as well as the relative L_{II} , L_{III} level widths of Cu and Zn as derived from their photoelectron spectra are presented. The results show that whereas the L_{III} /L_{II} photoelectron intensity ratios indicate that the initial vacancy distribution after x-ray photoionization is close to 2:1, the $L_3 M_{4,5} M_{4,5}$ /$L_2 M_{4,5} M_{4,5}$ Auger intensity ratios are much larger and undergo a sudden decrease at Z = 30. The level-width measurements show that the L_{III} widths are similar in Cu and Zn, but L_{II} width is greater in Cu than in Zn, contrary to the expected trend. These results give evidence that a great deal of vacancy reorganization has taken place following photoionization and prior to Auger emission. We interpret these reorganizations to be due to Coster-Kronig transitions f_{23}. These results are then compared with the theoretical calculations of Chen, Crasemann and Kostroun,[17] and agree with their predicted discontinuity at Z = 30 where f_{23} transitions become energetically impossible.

CONTENTS

ILLUSTRATIONS

INVESTIGATION OF LOW-Z COSTER-KRONIG TRANSITIONS BY MEANS OF AUGER AND PHOTOELECTRON SPECTROSCOPY

I. INTRODUCTION

When an atom is ionized in an inner shell it can deexcite either through radiative transitions with the emission of x-rays or through Auger transitions with the emission of electrons. Normally, in either mode of deexcitation the vacancy is filled by an electron from a major outer shell. However in some cases where it is energetically possible, the vacancy can be filled by an electron from a subshell of the same major shell and followed by the ejection of an outer shell electron. For example an L_I shell vacancy can be filled by an L_{III} shell electron with the ejection of a M_V electron. Such a transition is labelled as $L_1\ L_3\ M_5$ in analogy to ordinary Auger transitions. The existence of this special type of Auger transition was pointed out by Coster and Kronig[1] in 1935 to explain the anomalous behavior of the L-series x-ray spectra with respect to their intensity ratios, line widths and satellites.

Because of the Coster-Kronig transitions the initial vacancy distribution in L and M subshells can often be greatly disturbed prior to x-ray and Auger-electron emission so that one must take careful account of these transitions in the determination of higher shell fluorescence yields.[2] In the past few years ultra-high resolution Ge(Li) and Si(Li) detectors have made it possible to measure selectively K-x-ray — L-x-ray coincidences so as to deduce L_{II} and L_{III} subshell fluorescence and Coster-Kronig yields for $Z \geqslant 63$[3-15]. Concurrently, theoretical calculations on the radiative, Auger and Coster-Kronig transition rates for these subshells[16-22] have also become available for comparison with experimental results. However, even Si(Li) and Ge(Li) detectors do not at present possess sufficient resolutions to extend such coincidence measurements to the low-Z elements where the x-ray lines have small energy differences. On the other hand, electron spectroscopy with its high resolution capabilities should provide possible opportunities to observe the L- and M-shell Coster-Kronig spectra directly. Unfortunately, for low-Z elements, one is still beset with obstacles. Because the kinetic energies of the Coster-Kronig electrons are extremely low, (e.g., for $Z < 30$, $L_2\ L_3\ X$ transitions have kinetic energies less than 20 eV), the observation of these electrons in solid samples becomes very difficult due to energy losses and the interference of the intense secondary electrons from solids which also have energies in the same region. Consequently, direct observations of Coster-Kronig electrons have so far been limited to electron-excited gaseous samples such as Kr and Ar[23,24] and radioactive solid samples of heavy elements.[25,26] Due to these difficulties, experimental information concerning Coster-Kronig transitions at low Z has been extremely scarce if not non-existent.

But the high resolution of electron spectroscopy can be utilized in an alternate, albeit less direct, manner to study the Coster-Kronig transitions of low-Z solid materials. This involves the collateral information of the x-ray excited L-shell photoelectron spectra and the LMM Auger electron spectra. In what follows we will discuss our efforts in studying the behavior of the Coster-Kronig transition probability f_{23} in Co, Ni, Cu, and Zn ($27 \leqslant Z \leqslant 30$) by means of their L-shell Auger and photoelectron spectra. Our results will then be discussed in the light of the recent calculations of Chen, Crasemann and Kostroun.[17]

II. EXPERIMENTAL METHOD

The details of our x-ray photoelectron spectrometer have been reported elsewhere.[27] The entire assembly is situated in an oil-free vacuum system with an operating pressure of about 1×10^{-8} torr. Spec-pure foils of Co, Ni, Cu, and Zn were used as samples and Al $K_{\alpha_{1,2}}$ x-rays were used exclusively in these experiments as the exciting radiation. Because the electrons of interest originate from the top tens of angstroms of the sample surface, the samples were sputter-cleaned with Ar ions at 1.5 kV, 20 μm pressure, and a current density of about 0.2 ma/cm^2 in an antechamber prior to measurements. The time interval between the end of ion-sputtering and the beginning of analysis at 5×10^{-8} torr was about 6 minutes. An 11-cm radius hemispherical electrostatic spectrometer was used to analyze the electron energies. The resolution of the spectrometer was varied in these experiments between full-width-half-maximum of 1.55 eV and 2.0 eV for the Au $4f_{7/2}$ photoelectron line using Al $K_{\alpha_{1,2}}$ excitation. The coarser resolution was used to obtain the Auger spectra and those photoelectron spectra where intensity information was sought. The fine resolution was used to obtain the photoelectron spectra for relative level width measurements. The electrons were pulse-counted and their energy distribution was recorded on a multichannel analyzer operated in the multiscaler mode. Energy calibration of the Auger spectra was achieved by using the photoelectron lines from the same sample.[28] In this manner the work function of the spectrometer was implicitly taken into account.

III. RESULTS

In order to make use of part of the LMM Auger spectra in deducing the behavior of the Coster-Kronig transitions it is important to correctly identify the prominent features of the Auger spectra themselves. Until two years ago little experimental information existed concerning the outer shell Auger spectra of solids. In the last two years, however, a number of publications have appeared dealing specifically with the LMM Auger spectra of the first transition series,

i.e., $21 \leqslant Z \leqslant 30$[28-35] which include the elements of interest here. Some confusion arose over the correct identification of the most prominent LMM peaks in these metals. Whereas some investigators attributed these prominent peaks to vacancies in the L_{II} shell, i.e., L_2 MM Auger transitions[33-35], others assigned them to L_3 MM[28-32]. In view of the overwhelming evidence presented in references 28-32, there is little doubt that the L_3 MM assignment is the correct one. Figure 1 shows the detailed LMM spectra of Cu and Zn. We see that they are rather complex and rich in fine structures. We have tried to classify those numbered structures in terms of L-S coupling of the final outer-shell vacancies in another paper[36]. For the present purpose it suffices to note that by far the most prominent and definitive feature in both spectra is the $L_3\ M_{4,5}\ M_{4,5}$ group together with the accompanying $L_2\ M_{4,5}\ M_{4,5}$ lines. Therefore, in order to obtain information on the L_3 MM:L_2 MM intensity ratio which we are seeking in connection with the $L_2\ L_3$ X Coster-Kronig transitions, we have chosen to concentrate on the $L_3\ M_{4,5}\ M_{4,5}$ and $L_2\ M_{4,5}\ M_{4,5}$ region of the spectra.

Figure 2 shows the $L_3\ M_{4,5}\ M_{4,5}$ and $L_2\ M_{4,5}\ M_{4,5}$ portion of the LMM spectra of Co, Ni, Cu, and Zn. It is clear that:

1. The $L_3\ M_{4,5}\ M_{4,5}$:$L_2\ M_{4,5}\ M_{4,5}$ Auger intensity ratio is not constant among those elements,

2. Although precise numbers are difficult to extract from the data due to the irregular shape of the background, this intensity ratio varies roughly from about 6 or 7:1 in Co (Z = 27) and Ni (Z = 28) to about 5:1 in Cu (Z = 29), and undergoes a sudden decrease to about 3:1 in Zn (Z = 30),

3. Since all the spectra in Figure 2 are taken at the same spectrometer resolution it is obvious that the Auger lines in Co and Ni are quite a bit broader than those of Cu and Zn.

In contrast, the photoelectron spectrum of the L_{II} and L_{III} levels of Cu is shown in Figure 3. Here, the L_{III} :L_{II} photoelectron intensity ratio is about 2:1, definitely proportional to the electron population of these levels. Unlike the Auger intensity ratio, the L_{III} :L_{II} photoelectron intensity ratio remains constant at 2:1 for all four samples.

We have also measured the relative widths (full-width-half-maximum) of the L_{II} and L_{III} photoelectron lines of Cu and Zn at high resolution. The uncorrected results, which include the contributions from the Al $K_{a_{1,2}}$ line width of about 1 eV and instrumental width, are: 1.73 eV and 1.76 eV for the L_{III} level of Cu and Zn respectively, and 2.10 eV and 1.96 eV for the L_{II} level of Cu and Zn

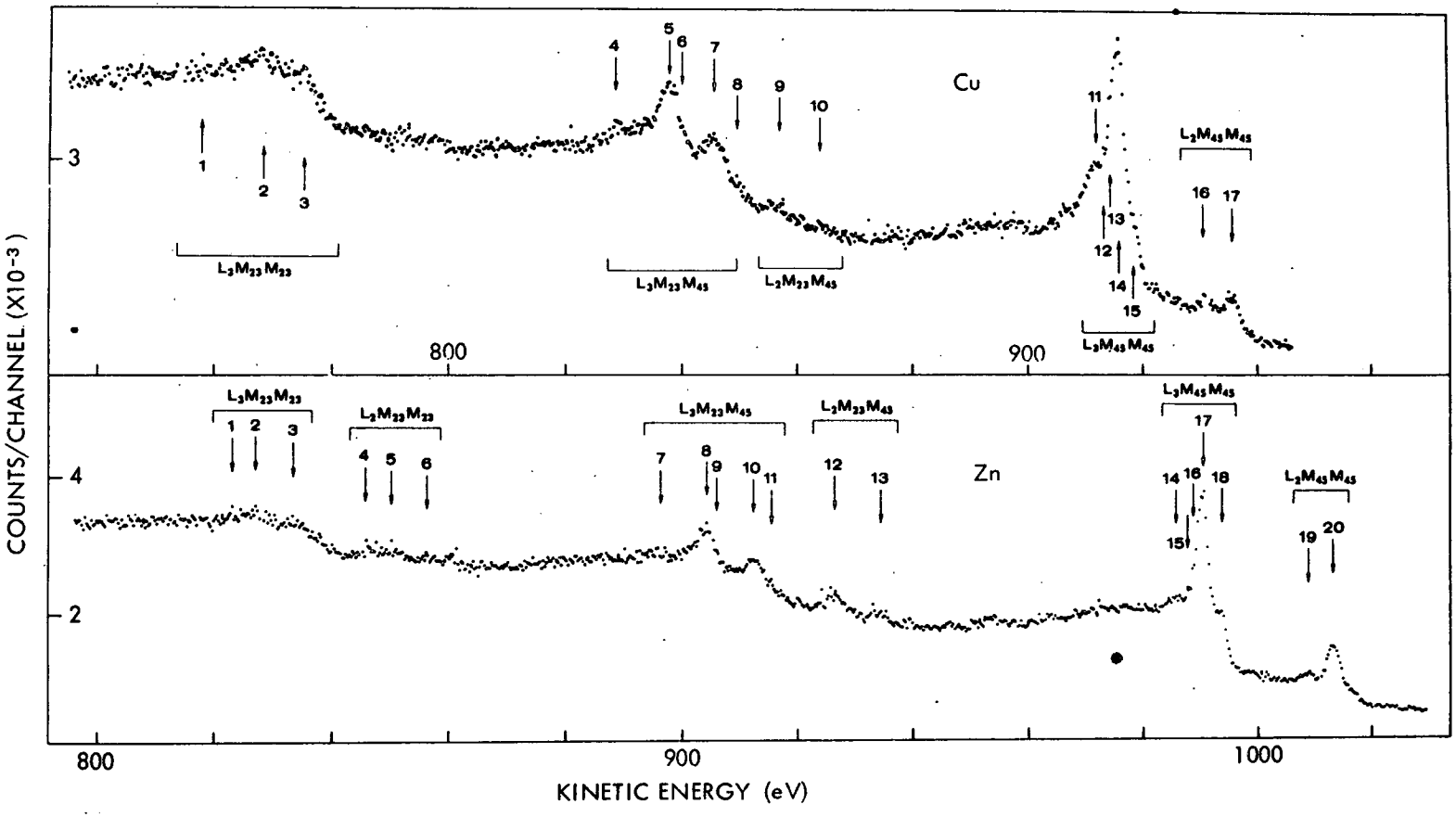

Figure 1. Detailed LMM Auger Spectra of Cu and Zn

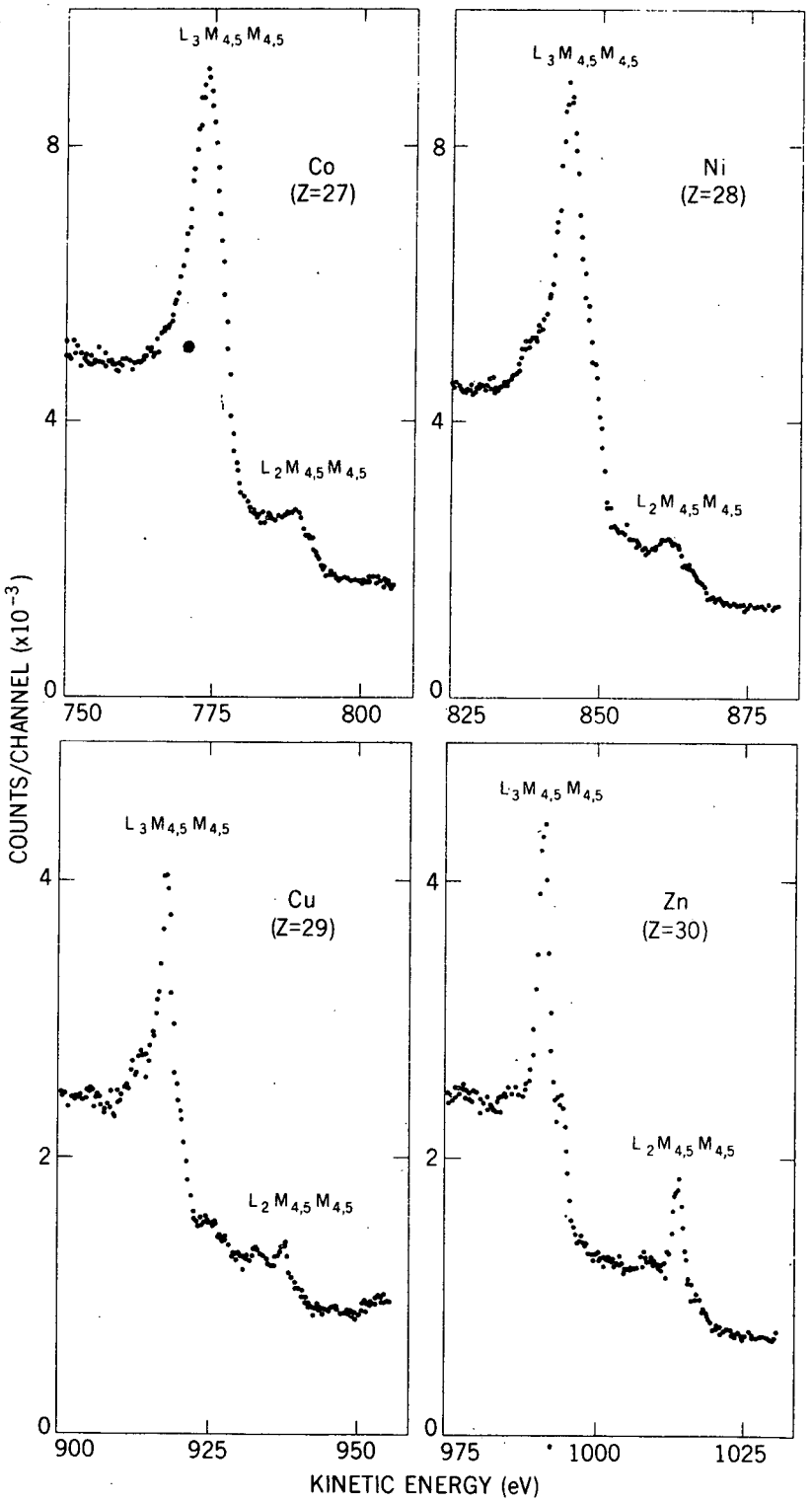

Figure 2. Portions of the LMM Auger Spectra of Co, Ni, Cu, and Zn Showing $L_3 M_{4,5} M_{4,5}$: $L_2 M_{4,5} M_{4,5}$ Intensity Ratios

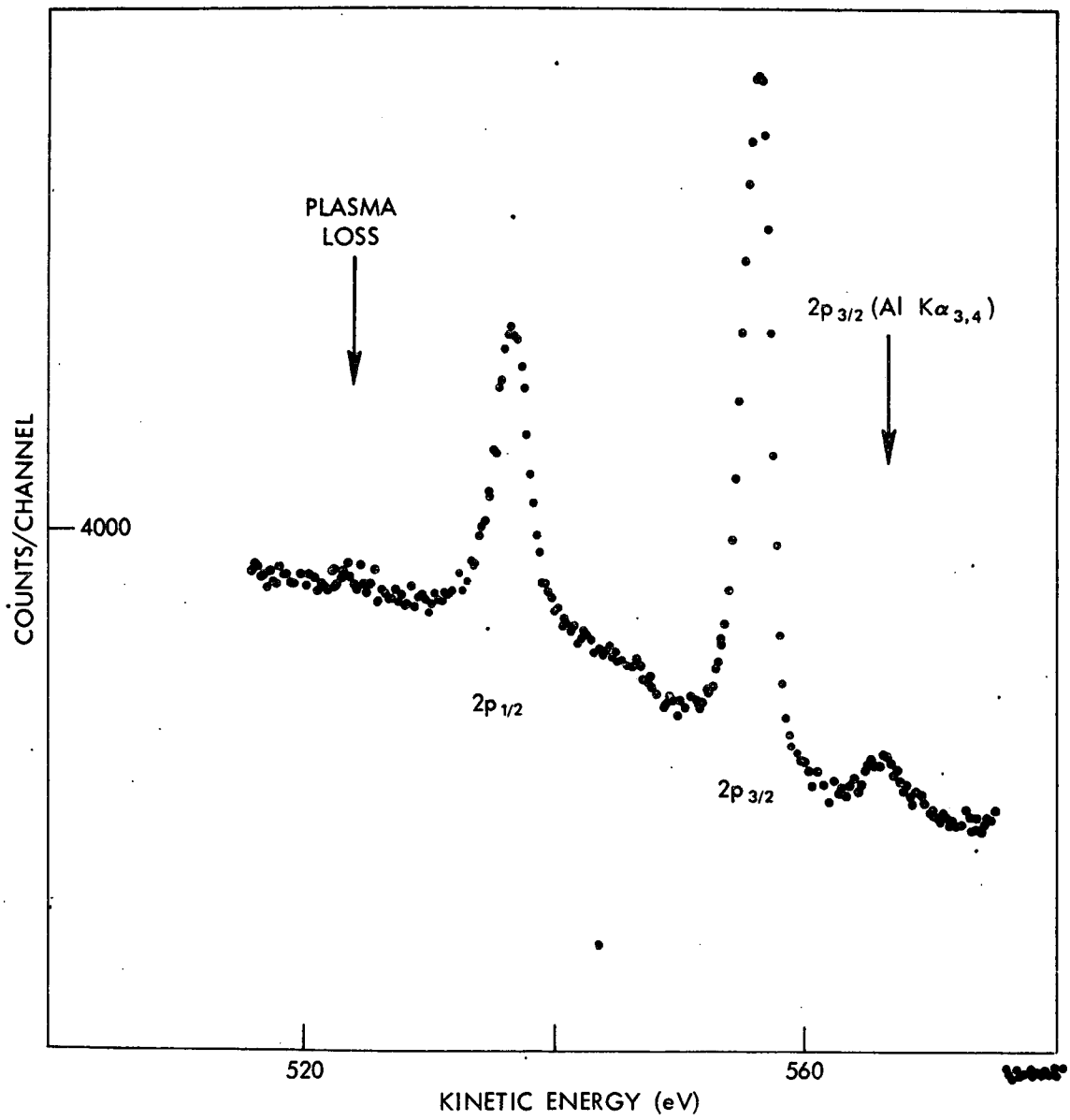

Figure 3. The L_{II}, L_{III} Photoelectron Spectrum of Cu Excited with Al $K\alpha_{1,2}$ x-rays

respectively. Since the contributions from the Al $K_{\alpha_{1,2}}$ line width and the instrumental width are constant it is seen that whereas the L_{III} level widths are almost equal between Cu and Zn (with Zn slightly larger), the L_{II} level width is greater in Cu (Z=29) than in Zn (Z=30), contrary to the expected trend as a function of Z.

IV. DISCUSSION

In the previous section we have presented our observations of the intensity ratios of both the Auger and photoelectron spectra for Co, Ni, Cu and Zn. In general one needs to be rather cautious in how one uses intensity ratios in electron spectra from solids. For example, the intensity of a photoelectron line depends on not only the photoelectric cross section of the shell or subshell from which the electron originates, but also the angular distribution of the ejected photoelectrons from that shell, the escape probability of such electrons from the sample with the ejected kinetic energy, and the detection efficiency of the spectrometer-detector system for electrons with this energy. Fortunately in our case where the L_{II} and L_{III} photoelectrons have almost equal kinetic energies, most of the factors mentioned above are also equal. Thus in this instance the relative L_{III} and L_{II} photoelectron intensities do give an indication of the relative photoelectric cross sections at the Al $K_{\alpha_{1,2}}$ x-ray energy, and hence, the relative initial vacancy distribution in the L_{III} and L_{II} shells immediately after photoionization. From our data this initial vacancy distribution in L_{III} and L_{II} shells is found to be about 2:1, proportional to the electron population ratio in these levels for all the four samples.

Since the kinetic energies of the $L_3 M_{4,5}$ $M_{4,5}$ and $L_2 M_{4,5}$ $M_{4,5}$ Auger lines are also almost equal, with identical separations as the L_{III}, L_{II} photoelectron lines, their escape probabilities from the sample and the instrumental detection efficiencies for them will again be quite similar. The intensities of these Auger lines will then depend on the following parameters:

1. The vacancy distribution in the L_{III} and L_{II} subshells at the time of Auger emission.

2. The fluorescence yields ω_3 and ω_2 for the L_{III} and L_{II} subshells, or as a corollary.

3. The Auger yields for these two subshells.

From the theoretical calculations of Chen et al.[17], McGuire[20], and Scofield[22], it is reasonable to assume that the fluorescence yields ω_3 and ω_2 are approximately equal in the same element, and both negligible compared to the respective Auger yields in this Z region. Furthermore, for all practical purposes, the

Auger yields for L_{III} and L_{II} subshells are also equal[17,21]. Therefore the $L_3\,M_{4,5}\,M_{4,5}$:$L_2\,M_{4,5}\,M_{4,5}$ intensity ratio essentially reflects the L_{III}:L_{II} vacancy ratio at the time of Auger emission. This being the case, the observed large $L_3\,M_{4,5}\,M_{4,5}$:$L_2\,M_{4,5}\,M_{4,5}$ ratios ($\gg 2$) in Figure 2 indicate that there has been a great deal of reorganization of vacancies subsequent to the photoionization of the L_{III} and L_{II} shells and prior to the emission of Auger electrons. A plausible mechanism responsible for such vacancy shifts is that of Coster-Kronig transitions.

It is known that where Coster-Kronig transitions are energetically possible their transition probabilities are much greater than the Auger transitions[2,23] so that a vacancy from a lower subshell can be shifted to a higher subshell before it is filled by an electron from another major shell. In the L shell there are three possible types of Coster-Kronig transitions with probabilities f_{12}, f_{13}, and f_{23}. f_{12} and f_{13} result in vacancy shifts from L_I shell to L_{II} and L_{III} shells respectively and f_{23} results in a vacancy shift from L_{II} to L_{III} shell. Calculations of Chen et al.[17], McGuire[20,21], and Callan[37] show that in the Z region of our interest f_{13} and f_{12} vary smoothly with Z, with a ratio f_{13}:f_{12} of about 2 for each element. Chen et al.[17] have further extended their calculations to include f_{23} in this region. Specifically, they showed that f_{23} experiences a sharp discontinuity around Z = 30 where such transitions become energetically impossible.

Our photoelectron spectra show that the L_I shell photoelectron intensity is much lower (by a factor of about 6) than that of L_{II} and L_{III}, implying substantially fewer initial vacancies in the L_I shell. Since both f_{13} and f_{12} vary smoothly with Z, with a constant ratio of about 2, there will be a small amount of vacancy shifts from L_I shell, with twice as many going to L_{III} shell than to L_{II} shell. These shifts will thus enhance somewhat the L_{III}:L_{II} vacancy ratio and hence the $L_3\,M_{4,5}\,M_{4,5}$:$L_2\,M_{4,5}\,M_{4,5}$ intensity ratio; but the amount of this enhancement will be nearly the same for Co, Ni, Cu, and Zn. Therefore, f_{13} and f_{12} transitions alone cannot explain either the large observed intensity ratio, or the discontinuity at Z = 30. These must therefore be due specifically to the f_{23} Coster-Kronig transition as predicted by Chen et al.[17]

The level width measurements in Cu and Zn provide additional evidence for the f_{23} transitions. As mentioned earlier, the L_{III} widths of Cu and Zn are similar but Cu (Z = 29) has a wider L_{II} level width than Zn (Z = 30). This anomalous decrease in L_{II} width as Z increases from 29 to 30 clearly indicates the presence of f_{23} in Cu and its sudden decrease in Zn.

V. CONCLUSIONS

Using Auger and photoelectron spectroscopy we have shown experimental evidence for the behavior of Coster-Kronig transitions f_{23} for low-Z elements. While the experimental results give qualitative support to the theoretical predictions of Chen, Crasemann, and Kostroun[17], the quantitative agreements are poor in several aspects:

1. Theoretical f_{23} contribution to the total L_{II} width is only about 10%. Judging from the large $L_3\ M_{4,5}\ M_{4,5}$:$L_2\ M_{4,5}\ M_{4,5}$ ratios the Coster-Kronig transitions seem to contribute a major portion of the L_{II} level width.

2. Although we are uncertain about our instrumental contribution to the width measurements (whether Lorentzian, Gaussian, or otherwise), the true L_{III}, width of Cu can be roughly estimated to be around 0.5 eV which is far smaller than the theoretical 1.41 eV. Similarly, the estimated true L_{II} width of Cu is about 1 eV as compared to the theoretical 1.54 eV. Revised calculations of Chen and Crasemann[38] will possibly bring better agreement between theory and experiment.

We think the broadness of the Auger lines in Co and Ni as compared to Cu and Zn is partially caused by the broadening of the L_{II} and L_{III} levels due to multiplet splitting[39] and partially due to the multiplicity of Auger states. Multiplet-splitting broadening is also the reason why only the level widths of Cu and Zn were measured and compared: both having filled 3d shells.

Similar experiments can be done on $L_{2,3}MM$:L_I MM Auger ratios and the L_I level widths to study f_{12} and f_{13} Coster-Kronig transitions. However, due to the lower photoelectric cross section and the high f_{12}, f_{13} transition probabilities, both the photoelectron line of L_I and the L_I MM Auger lines are very weak. Experimental observations of these lines are therefore much more difficult and contain large uncertainties.

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